BIO-BASED EPOXY/CLAY NANOCOMPOSITES AS A NEW MATRIX FOR CARBON FIBER REINFORCED COMPOSITES: THERMOPHYSICAL AND MECHANICAL PROPERTIES EVALUATION

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Abstract

The thermophysical properties of bio-based epoxy nanocomposites reinforced with organo-montmorillonite clay and the mechanical properties of carbon fiber reinforced plastics whose matrix is the bio-based epoxy/clay nanocomposites are reported. A novel sample preparation scheme was used to process the organically modified clay in the glassy bio-based epoxy network resulting in nanocomposites where the clay was homogeneously dispersed and completely exfoliated in the bio-based epoxy network. The storage modulus of bio-based epoxy at room temperature, which was below the glass transition temperature of the nanocomposites, increased approximately 0.9 GPa with the addition of 5.0 weight percent of exfoliated clay platelets. The glass transition temperature T_g decreased with addition of the organo-clay nanoplatelets. To understand the role of clay platelets in the bio-based epoxy nanocomposites, the microstructure of clay platelets were observed using transmission electron microscopy (TEM) and wide angle X-ray scattering (WAXS). Carbon fiber reinforced composites (CFRP) were processed using the bio-based epoxy/clay nanocomposites. No difference in elastic modulus and flexural strength was observed regardless of the use of different matrices. It was observed that the interlaminar shear strength of CFRP with bio-based epoxy was improved with adding 5.0 weight percent intercalated clay nanoparticles.

Introduction

The importance of environmentally friendly natural products for industrial applications has become radically clear in recent years with increasing emphasis on the environmental issues, waste disposal, and depleting non-renewable resources. Renewable resource-based polymers, having new advantage of eco-friendliness, can form a platform to substitute petroleum-based polymers through innovation in designing the new bio-based polymers and even at the sight of cost-performance. There is a growing urgency to develop and commercialize new bio-based products and other innovative technologies that can unhook widespread dependence on fossil fuel. Functionalized vegetable oils are now commercially available. Such functionalized vegetable oils find applications as coatings and plasticizer additives. More valuable applications of such epoxidized vegetable oils will give much return to agriculture thereby reducing the burden of petroleum-based products. The petroleum-derived epoxy resins are known for their superior tensile strength, high stiffness, and exceptional solvent resistance. Some of mechanical properties of epoxy resin can be improved by blending with functionalized vegetable oil. The blend of nanoscale reinforcements, such as organically modified clay, and bio-based epoxy resin could result in advanced materials applicable for automotive and aeronautic structures, when it is used with high-performance fibers, e.g. carbon fibers.

In the past studies, it was found that the petroleum-derived epoxy/clay nanocomposites have splendid characteristics, i.e. remarkably increased elastic modulus [1-6] and fracture toughness [7, 8]. The incorporation of bio-based glassy epoxy resins reinforced by nanoclay platelets, whose glass transition temperature is greater than room temperature, would be one of the best combinations for developing environmentally friendly nanocomposites. These developed bio-based nano-composites could satisfy the demanding requirements in different applications. In this paper, the properties of bio-based epoxy/clay nanocomposites and their carbon fiber reinforced plastics (CFRP) are investigated. The thermophysical properties of bio-based epoxy/clay nanocomposites were measured by dynamic mechanical analysis (DMA). The microstructure of the clay particles in the nanocomposites was observed by transmission electron microscopy (TEM) and wide angle X-ray scattering (WAXS). CFRP were processed using this newly-developed bio-based epoxy/clay hybrid nanocomposites matrix system.. The mechanical properties were measured with flexural and short beam shear tests.

Experimental Procedure

Materials

Bio-based Epoxy/Clay Nanocomposites: Diglycidyl ether of bisphenol F (DGEBF, Epon 862, Shell Chemicals Inc., epoxide equivalent weight=172) was used as main component. 30-80 weight percent of DGEBF was substituted by the same weight of functionalized vegetable oil (FVO), in various formulations and then cured with a proper curing agent. The amount of curing agent was theoretically calculated to maintain stoichiometry. Figure 1 is a schematic drawing of processing of bio-based epoxy/clay nanocomposites. To fabricate the anhydride-cured epoxy/clay nanocomposites, the 5.0 weight percent of organo-montmorillonite clay, Cloisite® 30B (Southern

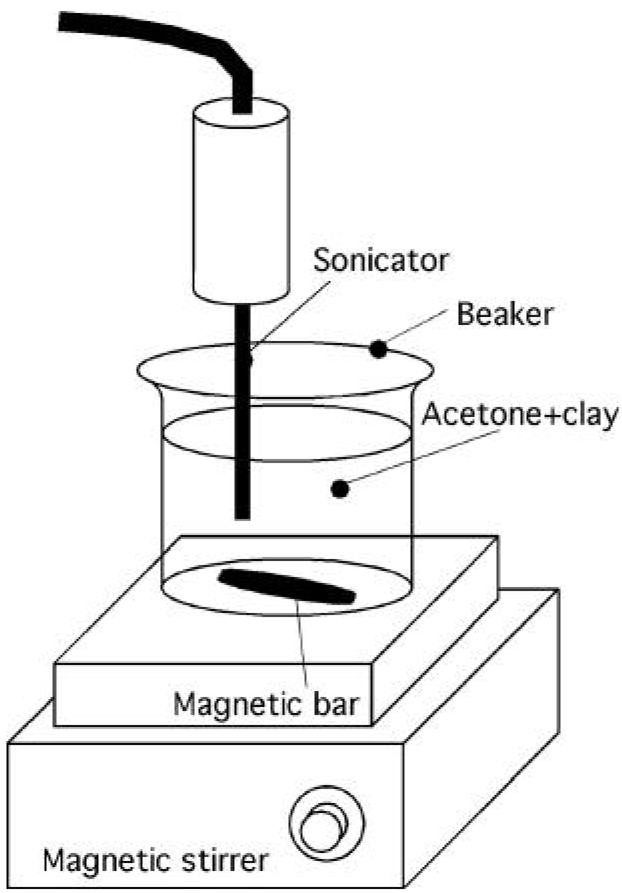

Fig. 1 Schematic drawing of sonication process of clay particles.

Clay Products), was sonicated in acetone for two hours using a solution concentration of more than 30 liters of acetone to 1 kilogram of clay, while it was constantly stirred by a magnetic stirrer. The epoxy resin and the functionalized vegetable oil was then added and mixed with a magnetic stirrer for an additional hour. The acetone was removed by vacuum extraction at approximately 100 ^{o}C for 24 hours, after which time the curing agent was blended in the solution with a magnetic stirrer. After mixing all components, the nanocomposites were cured at the suitable temperature.

Carbon Fiber Reinforced Plastics: Unidirectional carbon fiber fabric (Wabo® MBrace CF 130, Watson Bowman Acme Corp., Amherst, NY) was used as the reinforcement carbon fibers. MBrace CF 130 is manufactured from PAN-based carbon fibers (Torayca T 700, Toray, Japan). Four different matrices, pure DGEBF, neat bio-based epoxy with 50 weight percent FVO, 2.5 weight percent exfoliated clay nanocomposites with 50 weight percent of FVO, and 5.0 weight percent intercalated clay nanocomposites with 50 weight percent of FVO, were used to process CFRP. 2.5 weight percent exfoliated clay nanocomposites were processed by the same sonication method mentioned above. To fabricate 5.0 weight percent intercalated clay nanocomposites, organo-montmorillonite clay were simply added to DGEBF and FVO, and then mixed by a magnetic stirrer for an hour. These matrixes were coated on the unidirectional carbon fiber fabrics, and this was repeated to layup 10 layers. Finally, CFRP were processed by compression molding.

Morphological Characterization

Transmission Electron Microscopy: The exfoliated clay layers in the bio-based epoxy matrix were observed with transmission electron microscopy (TEM). Thin sections of approximately 100 nm were obtained at room temperature by ultramicrotomy with a diamond knife having an included angle of 4º. A JEOL 2010 TEM with field emission filament in 200 kV was used to collect bright field images of the bio-based epoxy/clay nanocomposites.

Wide-angle X-ray scattering: X-ray diffraction spectra were obtained with a Rigaku diffraction system (CuKα radiation with λ=0.15418 nm) having a monochrometer operating at 45 kV at room temperature. The diffractogram step size was 2θ=0.024°, a count time of 2.88 seconds and a 2θ range from 1 to 7°.

Thermophysical Characterization

Dynamic mechanical properties of bio-based neat epoxy and their clay nanocomposites were collected with a TA Instruments DMA 2980 operating in the three-point bending mode at an oscillation frequency of 1.0 Hz. Data were collected from ambient temperature to 150°C at a scanning rate of 2°C/min. A minimum of 3 specimens of each composition were tested. The grass transition temperature, T_g, was assigned as the temperature where loss factor, tan δ, was a maximum.

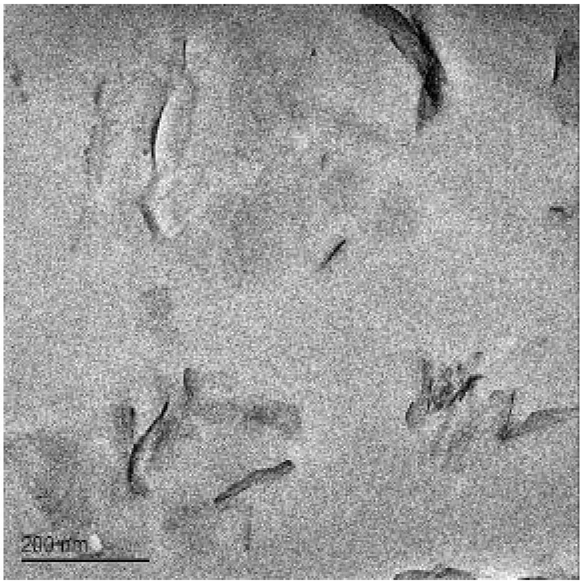

Fig. 2 Bright-field TEM micrographs revealing excellent exfoliation of clay platelets in epoxy matrix containing 30 wt.% functionalized vegetable oil.

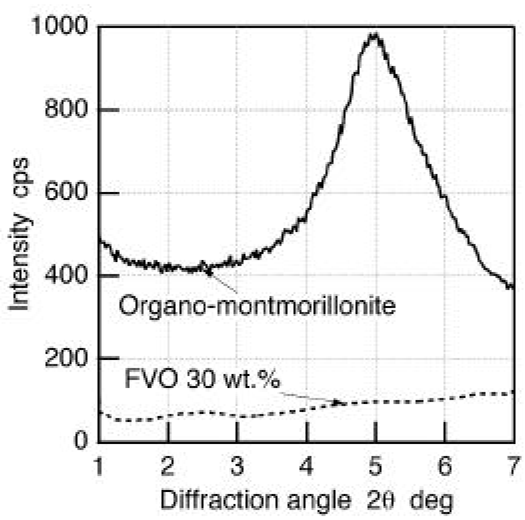

Fig. 3 WAXS patterns of organo-montmorillonite clay and bio-based epoxy/clay nanocomposites.

Mechanical Tests

Flexural tests were conducted to understand the mechanical properties of different CFRP. The flexural test specimens were cut into the size of 2.5 mm * 15 mm * 150 mm for measurements of elastic modulus and flexural strength. The span length between two supports was 127 mm. The crosshead velocity was 6.0 mm/min. The displacement at the loading point was measured by an extensometer. The short beam shear test specimens were cut into the size of 2.5 mm * 5.0 mm * 15 mm for measurements of interlaminar shear strength (ILSS). The span length between two supports was 10 mm. The crosshead velocity was 1.0 mm/min. A minimum of 3 specimens were used for both tests to reduce error.

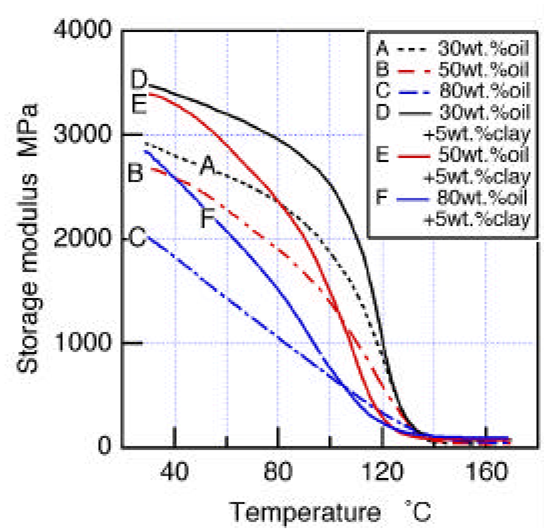

Fig. 4 Examples of the change of DMA curves of epoxy containing functionalized vegetable oil before and after adding 5.0 wt.% clay.

Results and Discussion

Morphology of clay platelets in bio-based epoxy matrix

Figure 2 shows the high magnification micrograph observed by transmission electron microscopy (TEM). In this figure, the view of perpendicular to the c-axis (i.e., along a-b plane) shows typical elongated fiber-like feature. It is extremely difficult to measure d-spacing because of the almost complete exfoliation and dispersion; only few clay platelets were stuck with each other. Particle size of clay platelets after the exfoliation was in the range between 50 and 200 nm on the a-b plane, which is absolutely smaller than the intercalated clay platelets [8]. It is because it is easier to break completely exfoliated clay platelets rather than intercalated clay sticking with a number of clay layers.

Figure 3 shows the WAXS patterns at low diffraction angles for organo-montmorillonite clay particles and several bio-based epoxy/clay nanocomposites prepared with the solution technique. The [001] diffraction of clay layers before the nanocomposite process appeared at $2q$=5.01°, therefore, the basal spacing of clay was determined to be 1.76 nm. On the other hand, no clear XRD peak for bio-based epoxy/clay nanocomposites was observed. Therefore it could be concluded from both the TEM micrograph and WAXS data that clay platelets were completely exfoliated. This excellent dispersion and exfoliation result in the higher elastic modulus of nanocomposites discussed in the following section.

Thermophysical properties

Figure 4 shows the change of storage modulus of bio-based neat epoxy and their 5.0 wt.% exfoliated organo-clay nanocomposites dependent on temperature. The storage modulus at room temperature, which was below the glass transition temperature of the bio-based

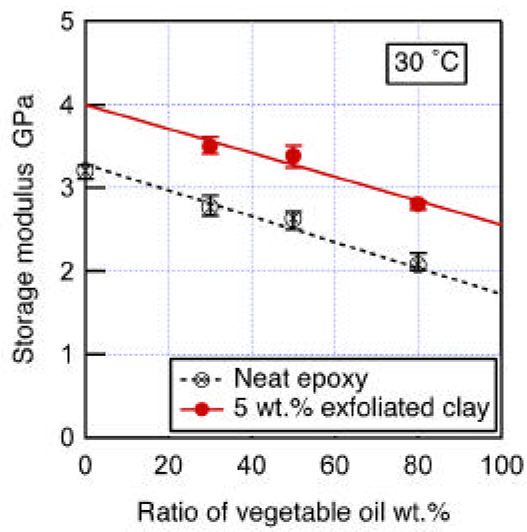

Fig. 5 Change of storage modulus of bio-based epoxy and their 5.0 wt.% exfoliated clay nanocomposites at 30 °C measured by DMA.

Table 1 Volume fraction of unidirectional CFRP processed by compression molding

	Volume fraction before curing	Volume fraction after curing
Epon 862	0.46	0.685
FVO 50	0.43	0.678
FVO 50 /Exfol. clay 2.5wt.%	0.405	0.667
FVO 50 /Inter. clay 5.0wt.%	0.369	0.632

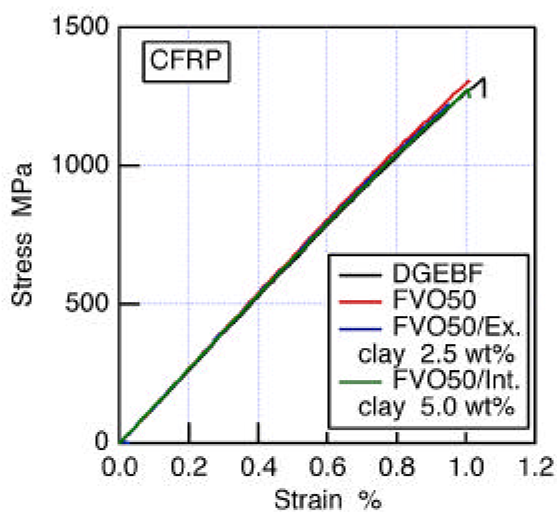

Fig. 6 Typical example of stress strain curve of unidirectional CFRP containing different epoxy matrix

epoxy/clay nanocomposites, clearly increased with the addition of 5.0 weight percent of organo-clay particle. Figure 5 shows the relation between the storage modulus at 30 °C and the amount of functionalized vegetable oil in the

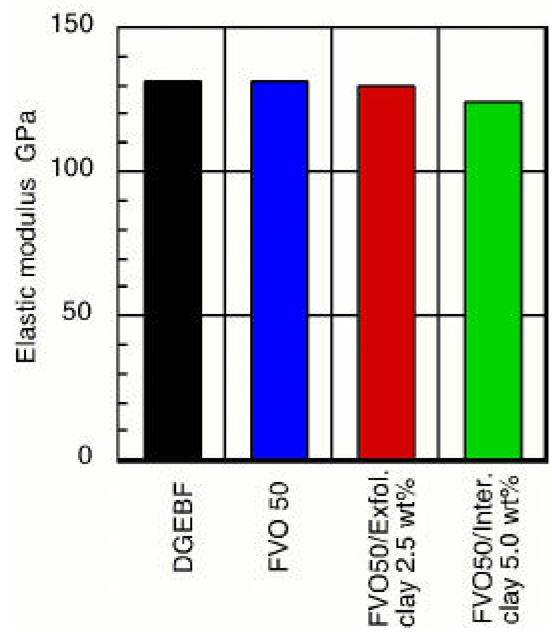

Fig. 7 Elastic modulus of unidirectional CFRP containing different epoxy matrix

neat epoxy and its clay nanocomposites. Solid and empty marks show bio-based neat epoxy and 5wt.% clay nanocomposites, respectively. It seems that the storage modulus of bio-based neat epoxy linearly decreased with increasing the amount of functionalized vegetable oil. The storage modulus of 5.0 wt. % clay nanocomposites showed approximately 0.9 GPa increase, comparing that of original bio-based neat epoxy. This reinforcing effect can be theoretically calculated with Tandon-Weng equation [9] for 3-D randomly oriented flake-reinforced composites.

Mechanical Properties of CFRP

Table 1 shows the volume fraction of carbon fibers in unidirectional CFRP before and after cure. First, the weight of carbon fiber fabric and the total weight of composites before and after cure were measured. The weight of the carbon fiber fabric is not changed; therefore, it is possible to estimate the weight of epoxy matrix before and after cure. The volume fraction of carbon fiber was then calculated with the density of both matrix and carbon fibers. In Table 1, it was confirmed that the different CFRP could be repeatedly processed with consistent final volume fraction of reinforcement carbon fibers.

Figure 6 shows the typical stress-strain curves of 4 different unidirectional CFRP. The stress and strain were theoretically calculated from the load and the displacement measured by an extensometer, respectively. Because of the consistent volume fraction of carbon fibers, the stress strain curves were almost the same, regardless of matrix. The CFRP did not show the plastic behavior in the stress-strain curves.

Figure 7 shows the comparison of elastic modulus of unidirectional CFRP containing different epoxy matrix.

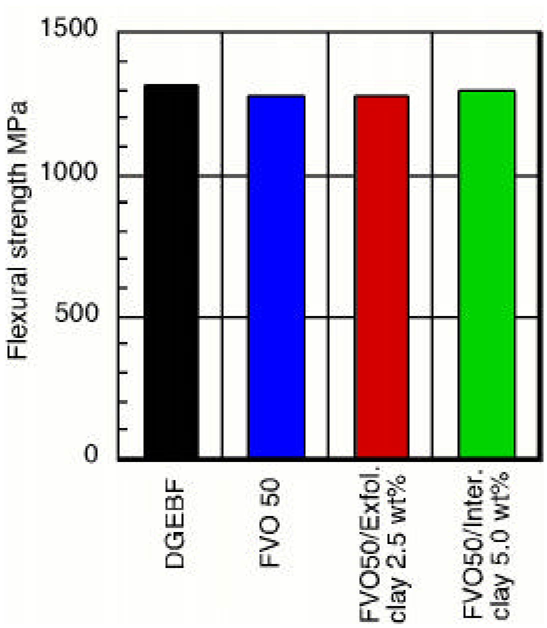

Fig. 8 Flexural strength of unidirectional CFRP containing different epoxy matrix

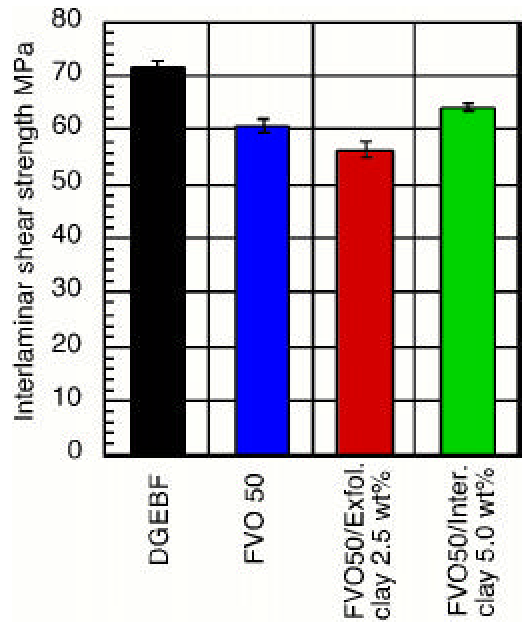

Fig. 9 Interlaminar shear strength of unidirectional CFRP containing different epoxy matrix

The modulus of unidirectional CFRP was consistent regardless of different epoxy matrix, because of almost the same volume fraction of carbon fibers. The values of the elastic modulus in this figure were slightly lower than the theoretical values calculated by the rule of mixtures, since the elastic modulus is underestimated by the flexural test because of the shear deformation [10].

Figure 8 shows the comparison of flexural strength of unidirectional CFRP containing different epoxy matrix. When the volume fraction of high-performance fibers is high, the strength of unidirectional FRP is dependent on the strength of the high-performance fibers. Therefore in this figure, the unidirectional CFRP containing different epoxy matrix showed nearly the same flexural strength. From the results of Figs. 7 and 8, it was confirmed that the bio-based epoxy would have a potential to apply for processing unidirectional or woven CFRP, which is useful for the structural application because of the same values of elastic modulus and flexural strength of CFRP.

Figure 9 shows the comparison of ILSS. The interlaminar failure occurs in the matrix phase or at the interface of resin/carbon fibers, therefore, this is the useful parameter to understand the matrix-dependent mechanical characteristics of unidirectional CFRP and the condition of adhesion at the resin/fiber interface. In Fig. 9, the CFRP having the neat DGEBF matrix showed highest ILSS. The ILSS of the CFRP having the neat bio-based epoxy matrix clearly showed the lower ILSS than that with neat DGEBF. This weaker property of the bio-based epoxy is a current problem for their use in structural application. When 2.5 weight percent exfoliated clay nanoplatelets were added to the bio-based epoxy, the ILSS decreased. In a contrast, when 5.0 weight percent intercalated clay platelets were added to the bio-based epoxy, the higher ILSS was observed in comparison to the neat bio-based epoxy. Therefore, it was possible to improve the properties with addition of clay particles with optimum extent of dispersion of clay particles in the epoxy matrix. Some of the authors [8] have already reported that with the petroleum based epoxy; the intercalated clay platelets improved the critical energy release rate although the exfoliated clay platelets marginally improved the fracture behavior. Therefore, it can be inferred that the result of short beam shear test showed similar trends as the fracture test of nanocomposites.

Conclusions

New nanocomposites from bio-based epoxy and organo-clay and further reinforcement of such biobased nanocomposite with carbon fibers result in novel advanced materials of very high modulus and strength properties. A novel sample preparation scheme was obviously effective to process the organically-modified clay in the glassy bio-based epoxy network resulting in nanocomposites where the clay was almost completely exfoliated by the bio-based epoxy network. The excellent exfoliation was confirmed by TEM and WAXS data. The processed exfoliated clay nanocomposites showed higher storage modulus as compared to the bio-based neat epoxy containing the same amount of functionalized vegetable oils. Therefore, the lost storage modulus with higher amount of functionalized vegetable oils can be regained with exfoliated clay reinforcement. CFRP were processed using the bio-based epoxy/clay nanocomposites. No difference in elastic modulus and flexural strength was observed regardless of different matrices, because of high volume fraction of the reinforcement carbon fibers. It was observed that the ILSS of CFRP with bio-based epoxy was improved with adding 5.0 weight percent intercalated clay nanoparticles.

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